FINAL

PCB ANALYSIS AND RISK ASSESSMENT AT NAVY INSTALLATIONS

Part A: Overview of PCB Mixtures

Part B: PCB Human Health Risk Assessment

Part C: PCB Ecological Risk Assessment

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EXECUTIVE SUMMARY

Environmental restoration investigations and risk management decisions at Navy installations potentially contaminated with PCBs are complex. This document presents a cost-effective, expeditious, tiered process for PCB sampling and analysis and conducting Human Health and Ecological Risk Assessments (referred to as HHRA and ERA, respectively). This framework will provide project managers with the necessary PCB data to make informed risk management decisions regarding remediation or clean closure for property transfer. The goal of this document is to provide an overall framework starting with site screening and ending with a comprehensive and detailed HHRA and ERA if warranted.

For ease of use and clarity for the remedial project manager (RPM), this document has been subdivided into three parts:

- *Part A:* Overview of PCBs;
- *Part B:* Calculating Human Health Risks For PBC Sites; and
- *Part C:* Ecological Risk Assessment for PCB Sites.

Part A presents background information on PCB mixtures (PCBs), emphasizing the complexity of both the original commercial product and environmental PCB mixtures that have undergone weathering. Developing a sampling and analysis plan for PCB sites can be technically difficult and costly due to the complexity of Aroclor mixtures, degree of environmental weathering, cost of analyses, and number of analytical options available. This part of the document presents a tiered sampling and analysis framework for developing a focused sampling plan. The goal is to extract maximum information for the least cost at each step of the investigation. Different methods are compared with regard to cost and utility. Background information is presented to describe the pertinent aspects of laboratory analysis of three general categories of PCB mixtures that are typically performed—namely, Aroclors, PCB homologues, and PCB congeners. The latter group includes the 13 dioxin-like PCB congeners, which are important for HHRA and ERA. PCB fate and transport information is briefly presented to highlight differences in composition between a commercial PCB mixture (Aroclor) and the weathered PCB commercial mixtures to assist the RPM in identifying specific environmental media that need to be sampled. Confounding factors such as the presence of minute contaminant of dioxin-like furans in commercial Aroclors, which are inadvertently generated during manufacturing, are discussed as it pertains to HRRA and ERA. Information to prevent overestimating and underestimating PCB contamination and concomitant HRRA and ERA risks is also presented.

Part B presents an overview of PCB analyses as it relates to conducting a human health risk assessment (HHRA). This information closely follows U.S. EPA PCB guidance and the National Research Council, National Academy of Sciences. It describes the type of PCB data that is used for a HHRA within a tiered approach. In particular, guidance is provided for when it is appropriate or advisable to use Aroclor, PCB homologue, or PCB congener data. The toxicity of PCBs is discussed based on the type of contaminated environmental media and exposure routes, rather than type of Aroclor originally released.

Part C presents information on how to conduct a PCB-based ecological risk assessment (ERA). PCB toxicity to aquatic organisms, amphibians and reptiles, birds, and mammals is discussed for both Aroclor and PCB congeners. The framework for the ERA is presented with the goal of making cost-effective risk management decisions.

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PART A: OVERVIEW OF PCBs

1.0 INTRODUCTION

1.1 PCBs As Complex Mixtures

Polychlorinated biphenyls (PCBs) refer to complex man-made mixtures of chlorinated hydrocarbons. (polychlorinated biphenyls) were specifically manufactured for their insulating properties and have historically been used in capacitors, transformers, and other electrical equipment as they do not easily burn, evaporate nor conduct electricity. PCBs are usually thick, oily liquids that are clear or yellow in color and have no odor and are mostly insoluble in water. Although numerous PCB mixtures were manufactured in many countries, all PCBs produced in North America were made by a single producer, Monsanto Corporation and are referred to as Aroclors. Aroclors are the primary focus of this document because with few exceptions the Navy's PCB sites involved uncontrolled releases of Aroclors. Additionally, the nomenclature most frequently used at PCB sites is based on the Aroclor numbering system. Finally, the PCB analytical methods developed by U.S. EPA are based on the composition of commercial Aroclor mixtures.

The term "Aroclor" refers to a PCB mixture of individual PCB compounds called PCB congeners. Theoretically, Aroclor mixtures can contain up to 209 different individual PCB congeners; however, most Aroclors contain only about 130 individual congeners (Safe 1990). In formulating and manufacturing Aroclors, Monsanto developed a numbering system to identify an individual PCB mixture that would exhibit a particular physical property, rather than a particular chemical composition. The physical properties of Aroclor mixtures are governed by the extent of chlorination in the individual PCB congeners. This is reflected in the numbering system. All Aroclors are numbered with a 4-digit code where the first two digits are 12 and the last two digits represent the percentage by weight of chlorine. For example, Aroclor 1260 is a mixture of more than a hundred individual PCB congeners in which the mixture is 60 percent (by weight) chlorine, which is a highly chlorinated mixture. In contrast, Aroclor 1242 is only 42 percent chlorine [The only exception to this numbering system is Aroclor 1016, which is a special distillation product of Aroclor 1242 that contains only 1 percent of PCB congeners with 5 or more chlorines.]. Table A-1 presents the homologue groups present in different Aroclors together with the corresponding weight percentage.

Groups of individual PCB congeners having the same *number* of chlorines are called PCB homologues. For example, the group of PCB homologues referred to as monochlorinated biphenyls has only one chlorine to the biphenyl ring while the hexachlorinated biphenyl homologue group has six chlorines. Despite the complexity and variability of Aroclor mixtures, different Aroclor mixtures have many individual homologues in common. Table A-1 shows the overlap of common PCB congeners that are present in Aroclors.

Table A-1. Common Pcb Homologue Groups In Each Aroclor

HOMOLOGUE GROUPS (Groups of congeners with same number of chlorines)	Chlorine (Weight Percent)	AROCLOR MIXTURE						
		1221	1232	1016	1242	1248	1254	1260
Biphenyl-No Chlorines (0)	0 (1)	10	-	-	-	-	-	-
Mono-Chlorinated Biphenyls (1)	18.8 (1)	50	26	2	3	-	-	-
Di-Chlorinated Biphenyls (2)	31.81 (1)	35	29	19	13	2	-	-
Tri-Chlorinated Biphenyls (3)	41.3 (1)	4	24	57	28	18	-	-
Tetra-Chlorinated Biphenyls (4)	48.61 (1)	1	15	22	30	40	11	-
Penta-Chlorinated Biphenyls (5)	54.4 (1)	-	-	-	22	36	49	12
Hexa-Chlorinated Biphenyls (6)	59 (1)	-	-	-	4	4	34	38
Hepta-Chlorinated Biphenyls (7)	62.8 (1)	-	-	-		-	6	41
Octa-Chlorinated Biphenyls (8)	66 (1)	-	-	-	-	-	-	8
Nona-Chlorinated Biphenyls (9)	68.8 (1)	-	-	-	-	-	-	1
Deca-Chlorinated Biphenyls (10)	-	-	-	-	-	-	-	-

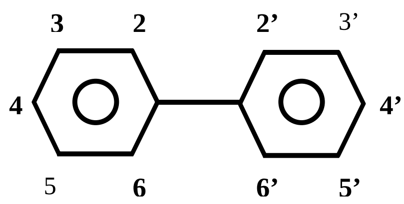
Note (1): Homologues are in weight percentages.
Number in parentheses indicates the number of chlorines in the homologue group.

The toxicity of a particular PCB mixture, whether it is the original commercial Aroclor or weathered environmental mixture analyzed in a sample, is dependent on the type and quantity of individual PCB congeners present in the PCB mixture. Although information on homologue composition can provide general information, it does not provide congener-specific information that is necessary to quantify toxicity and potential risks. This is because the toxicity of specific individual PCB congeners *within* each homologue group can vary by several orders of magnitude. In other words, knowledge of the homologue composition is not particularly useful in quantifying the toxicity of the PCB mixture. While the *number* of chlorines represented in each homologue group is important, it is the three-dimensional *position* of chlorines and the conformation of the biphenyl rings that ultimately govern the toxicity of each of the 209 PCB congeners. Thus, it is not possible to assign toxicity values to homologue groups.

The overall toxicity of a particular PCB mixture is the *sum* of the congener-specific toxicity contributed by each individual congener (which is typically number more than 100). As mentioned above, environmental weathering can dramatically alter the PCB congener composition of the originally released commercial Aroclor and, consequently, the toxicity. Therefore, to evaluate the toxicity and health risks associated with environmental PCB mixtures, the composition and concentration of individual PCB *congeners* must be quantified. Appendix A presents the weight percent of each of the 209 congeners in commercial Aroclors.

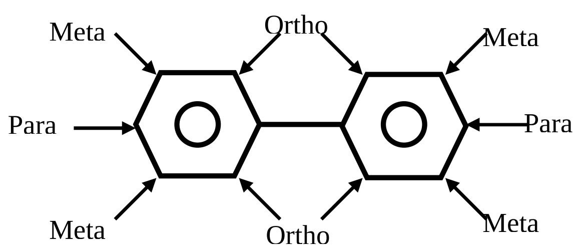
PCB congener chemical notation indicates specific positions where the chlorines are attached to the biphenyl ring as indicated in Figure A-1. For example, the PCB congener designated 2,3,4,2', 3', 5'-hexachlorobiphenyl has six chlorines attached to the biphenyl ring in positions 2,3 and 4 of one phenyl ring and 2, 3 and 5 of the other. The International Union of Pure and Applied Chemists (IUPAC) have developed a more simplistic system. With this system individual PCB congeners are assigned a number ranging from 1 to 209 (as indicated in Appendix A). For example, 2,2', 5,5'-tetraphenyl is PCB congener number 52 (or PCB-52).

Figure A-1. Positions where Chlorines are attached to the Biphenyl Ring



As noted, the positions of chlorination on the biphenyl ring govern its toxicity. Of most importance are positions 2, 6, 2', and 6', which are the carbons nearest the bond between phenyl rings because these are referred to as *ortho* positions (positions 3, 5, 3', and 5' are *meta* positions while 4 and 4' are *para* positions) (see Figure A-2). Chlorinated ortho positions are important because they prevent coplanar alignment. This can be envisioned as two flat pancakes lying on a flat surface representing the two biphenyl rings that are flat and parallel.

Figure A-2. Biphenyl Ring showing Ortho, Meta and Para Chlorine substitution positions.



Non-ortho chlorinated PCB congeners can assume a flat planar configuration that is similar to the rigidly planar configuration of dioxins and furans. All flat planar PCB, dioxins, and furans elicit the identical toxic responses and are therefore, referred to as having "dioxin-like" toxicity. There are 13 coplanar dioxin-like PCB congeners that may be present in some Aroclor mixtures. These 13 pose significantly greater toxicity and health risks compared with non-dioxin-like PCBs.

For the most part, PCBs detected at Navy installations were released as commercial Aroclors. However, PCB congeners can also be inadvertently generated "*de novo*" (newly produced) by burning chlorine-containing chemicals or by incineration of industrial or municipal waste. At sites where PCBs are suspected to have been generated *de novo,* Aroclor analysis cannot be used to characterize the site. PCBs generated *de novo* will not have an Aroclor "fingerprint," which is used by the analytical chemist to identify Aroclors. Each Aroclor fingerprint is unique and is based on the relative proportion of individual PCB congeners in the mixture. While PCBs generated *de novo* will not have an Aroclor fingerprint, they will have a unique fingerprint which will be defined by combustion conditions, including combustion temperature, feedstock, chlorine content, oxygen, etc.

> Note: When there is a suspicion that PCBs were generated de novo from combustion activities, PCB congener analysis should always be performed.

2.0 LABORATORY ANALYSES USED TO CHARACTERIZE PCB MIXTURES

PCB analyses range from simple field screening methods, which are used to confirm the presence or absence of PCBs, to sophisticated methods that quantify each of the 209 individual congeners that may be present in the parts per quadrillion range. Most PCB analyses routinely performed on environmental samples rely on similar gas chromatography techniques that separate groups of similar PCBs or individual PCB congeners based on volatility and polarization. Each method has advantages and disadvantages regarding sampling and analytical cost, turnaround times, chemical specificity, detection limits, and use in an HHRA or ERA.

Choosing an analytical method for quantifying PCB concentrations in soil, sediment, water, and biota can be confusing. This is because there are approximately 17 different USEPA PCB analyses (not including variations of each analysis). Each analysis has been developed to quantify the concentration of either aroclor, homologue, or congener. The selection of the particular analysis is based on the purpose of the investigation and particular goals of the project team.

Table A-2, developed by the nrc (nrc 2001), summarizes the cost benefit of conducting pcb analysis for the three different types of analytes; namely, aroclor, homologue, and pcb congener. Note that the table combines aroclor and homologue analyses because they have similar utility and cost-benefit properties.

Table A-2. Comparing Relative Cost And Utility: Aroclor and Homologue versus PCB-Congener Specific Analyses

ANALYTE	COST	HIGH UTILITY	LOW UTILITY
Aroclor or Homologue Analysis	**Low**	**Characterizing Recent Non-Weathered Aroclor Release**	**Biological Samples** **Weathered PCBs**
		Preliminary Site Screening: ***Soil***	
		Preliminary Site Screening: ***Sediment***	
		PCB Quantification	
		Soils and Sediments	
		a. Single PCB Mixture	
		b. Low Organic Carbon	
		c. Short Residence Time	
PCB Congener Method	**High**	**Biological Samples**	
		Weathered PCBs	
		Data Utilized for Toxicology Analysis	

Note: table is from NRC 2001.
Aroclor and homologue analyses are different analyte groups but are grouped together because they share the same features.

As indicated in Table A-2, there are advantages and disadvantages to Aroclor/homologue and PCB congener analysis. Most notably, Aroclor/homologue analysis is considerably less expensive than PCB congener analysis; however, it does not provide detailed congener-specific information that may be necessary for the intended investigation. In contrast, PCB congener analysis provides highly detailed congener data, which is necessary for weathered mixtures, but the costs may be prohibitive for some sites. The sampling and analysis plan should consider the advantages of both types of PCB analytical methods for both short- and long-term objectives. Another reason to carefully design a sampling and analysis plan is that it may not be possible to pool or combine Aroclor, PCB homologue, and congener data sets for statistical analyses or risk assessments. Sampling efforts could be wasted if sampling was determined to be inadequate midway through an investigation. It is most cost effective to implement an iterative sampling plan where a limited number of samples are collected and the data evaluated before subsequent sampling and analysis of a much large number of samples. Such an approach will preclude extensive re-sampling of the same locations using a different analytical approach.

As previously noted, costs associated with PCB analyses range from inexpensive Aroclor analysis to expensive PCB congener analysis ($900 to $1,200 per sample). Therefore, as part of an iterative or tiered approach, sites can be cost-effectively screened with a limited number of inexpensive Aroclor analyses, and subsequent sampling with more expensive PCB congener analysis can be conducted as warranted. Table A-3 is a decision-making flow chart that can be used as a framework for developing a comprehensive PCB sampling and analysis plan. It should be noted that, historically, it was appropriate to screen sites as well as estimate site risks based on Aroclor data for both the HHRA and ERA. However, more recent guidance requires that much more detailed information on PCB congener data be collected at PCB-contaminated sites. The first step in the tiered approach is to determine if the suspected PCB contamination is the result of Aroclors being released or *de novo* generation from combustion of organic materials in the presence of chlorine. [It is also important to decide whether target remediation levels will be based on potential risks or applicable or relevant and appropriate related (ARARs) requirements such as the Toxic Substance Control Act (TSCA)]. Because most Navy sites will involve Aroclor releases, Aroclor analysis can typically be used as a preliminary screen and to investigate the nature and extent of contamination where the spatial extent of the release is determined. The results of the Aroclor analysis, however, must be interpreted cautiously because preliminary data indicating no contamination may be a false negative result. This is particularly true when the PCB mixture has undergone extensive weathering (or has been formed *de novo*). To confirm no PCB congeners are present, it will be necessary to conduct homologue or congener analysis on a limited number of samples. This confirmation sampling will provide information on groups or individual PCB congeners that Aroclor analysis cannot. For example, it is possible to have Aroclors non-detected but have dioxin-like PCB congeners present at levels that pose unacceptable human health and/or ecological risks.

Note: If penta-, hexa-, or hepta- PCB homologue groups are detected, PCB congener analysis should be performed for a limited number of samples to determine if dioxin-like PCB congeners (which fall into these three homologue groups) are present.

As a cost-saving step, PCB congener analysis need only be conducted on a small number of samples to determine whether a statistically significant correlation exists between the *total* PCB concentration (based on Aroclor or homologue analysis) and the "group of PCB congeners of interest," which typically includes the dioxin-like PCB congeners. Quantifying a strong correlation will permit the use of Aroclor or homologue data to serve as proxy data to estimate the concentration of dioxin-like PCB congeners. Using linear regression/residual analysis will provide the site-specific mathematical relationship between the concentration of total PCBs and PCB congener to be defined (this correlation statistical approach has been successfully used at numerous sites and will be developed by the Navy and included as an appendix in an updated revision of the this document). Correlation analysis can be used to: (1) Determine whether the correlation coefficient between the total PCB and dioxin-like PCB congeners indicates a strong correlation exists, and (2) Derive the mathematical relationship (represented by the equation of the line) between the total PCB concentration and PCB congeners. This cost-effective analysis requires only a limited number of PCB congener analyses be conducted to establish a correlation between total PCBs and the subgroup of dioxin-like PCB congeners. After establishing a strong correlation exists, PCB analyses can be shifted back to the less expensive Aroclor or PCB homologue analysis. The dioxin-like PCB congener concentrations can then be estimated based on total PCB concentrations.

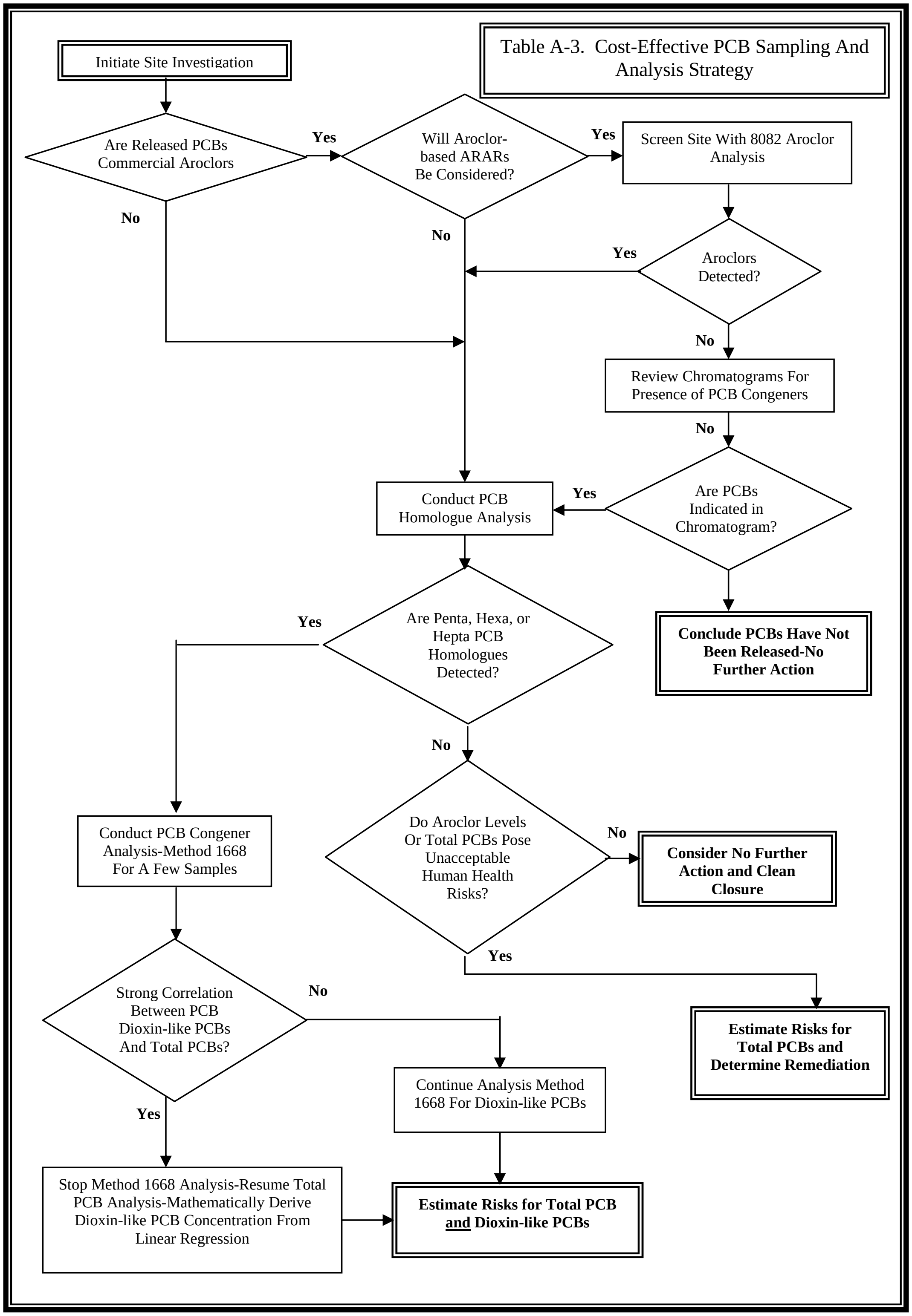


Table A-3. Cost-Effective PCB Sampling And Analysis Strategy
Initiate Site Investigation
Are Released PCBs Commercial Aroclors
Yes
No
Will Aroclor-based ARARs Be Considered?
Yes
No
Screen Site With 8082 Aroclor Analysis
Aroclors Detected?
Yes
No
Review Chromatograms For Presence of PCB Congeners
No
Are PCBs Indicated in Chromatogram?
Yes
Conduct PCB Homologue Analysis
Conclude PCBs Have Not Been Released-No Further Action
Are Penta, Hexa, or Hepta PCB Homologues Detected?
Yes
No
Conduct PCB Congener Analysis-Method 1668 For A Few Samples
Do Aroclor Levels Or Total PCBs Pose Unacceptable Human Health Risks?
No
Consider No Further Action and Clean Closure
Yes
Estimate Risks for Total PCBs and Determine Remediation
Strong Correlation Between PCB Dioxin-like PCBs And Total PCBs?
No
Yes
Continue Analysis Method 1668 For Dioxin-like PCBs
Stop Method 1668 Analysis-Resume Total PCB Analysis-Mathematically Derive Dioxin-like PCB Concentration From Linear Regression
Estimate Risks for Total PCB and Dioxin-like PCBs

2.1 Aroclor Analysis

Historically, samples collected at PCB-contaminated sites have been quantified by Aroclor analysis. However, at most sites currently being investigated Aroclor data fall far short of meeting today's data requirements for conducting an HRRA or ERA. The use of Aroclor data in environmental restoration should be limited to the following:

- Initial site screening to determine whether a commercial Aroclor release has occurred:
- Determine type(s) of Aroclors (e.g., Aroclor 1016, 1260, etc.) historically released;
- To develop a correlation between total Aroclors and specific (carcinogenic) PCB congeners;
- To determine the amount of weathering that has occurred; and
- When clean-up or presumptive remedy is based upon Aroclor results.

Using Aroclor analysis in the initial phase of site investigations (during preliminary site screening) to determine if PCBs have been release is quick, efficient, and cost-effective. Aroclor analysis averages approximately $200-$400 per sample (Appendix A), and the laboratory analytical turn-around times are typically short. However, the project team should carefully evaluate Aroclor analytical data because it may provide "false negative" results. An analytical chemist should be included as part of the project team to carefully evaluate samples reported as "non-detects" before automatically concluding a sample contains no PCBs. False negative errors can result from subjective judgments by the laboratory chemist when they interpret sample chromatograms from an environmental medium because they compare the sample chromatogram with reference chromatograms for commercial Aroclor laboratory standards. Frequently, chromatograms from environmental samples (where the Aroclor composition has been altered by weathering) do not resemble the original Aroclor mixture originally released. For example, characteristic peaks representing homologue groups may be missing due to degradation or environmental transport. The absence of these homologue groups in the sample chromatograms may result in the chemist concluding a particular Aroclor may not be present.

The degree to which commercial Aroclor mixtures undergo weathering is dependent on many factors, including the amount of PCBs released, the type of Aroclor released, differential degradation, and the physical-chemical properties of each environmental media (e.g., pH, organic content, moisture content, temperature, etc.). <u>It should be stressed that weathering of PCB mixtures is selective, preferentially affecting particular congeners.</u> For example, less-chlorinated PCB congeners are more water-soluble than more-chlorinated congeners and may migrate from the site of the initial PCB release via runoff or leaching. Less-chlorinated PCB congeners may also be more readily degraded through biodegradation compared with more highly chlorinated congeners. With few exceptions, PCBs mixtures at Navy sites have undergone extensive weathering and the characteristic peaks in site and reference chromatograms may not match up.

Consequently, the laboratory analyst may report Aroclors in the sample as non-detect, and the project team chemist should request the laboratory to review chromatograms for the presence of any PCB congeners.

Another source of negative bias in Aroclor analysis occurs when Aroclor 1268 is present in the site sample as part of the historical release (see NRC 2001). This is because decachlorobiphenyl (DCB; PCB 209) is added as an internal standard (because PCB 209 has the highest molecular weight of all congeners and will elute beyond all other congeners), and commercial mixtures of Aroclor 1268 contain approximately 4.8 percent PCB 209. According to NRC (2001): *"Thus, the recovery and GC response of PCB 209 might not be representative, and its use as an internal standard might lead to a higher degree of imprecision compared with the NOAA method."*

The last reason project managers should exercise caution when Aroclor analysis is used exclusively to investigate PCB sites is that PCB commercial mixtures contain significant amounts of polychlorinated dibenzofurans (CDFs) and polychlorinated naphthalenes (PCNs). While PCNs have been shown to produce similar toxicity to the less-toxic PCBs, some CDF congeners are exceedingly carcinogenic. If no independent analysis is conducted for these contaminants, the extent of contamination related to PCB releases may be underestimated. More information on this issue is presented in Section 1.2.5.

In contrast to the negative bias Aroclor analysis may introduce, relying exclusively on Aroclor analysis can lead to *overestimating* total PCBs in environmental samples if more than one Aroclor is present in the sample. This is because individual PCB congeners common to different Aroclors can be counted twice or more depending on the number of Aroclors present in the sample.

Despite the drawbacks associated with Aroclor analysis, it is typically used to screen sites for the presence of PCBs due to its low cost when the project team needs to roughly define the area(s) of contamination. Aroclor analysis can also be used when ARARs (e.g., TSCA) may be used to set target remediation levels. Aroclor analytical method *EPA SW 846 Method 8082/PCBs*, which is based on gas chromatography, is the preferred method for sites suspected of a commercial Aroclor release. With this method, Aroclors 1016, 1221, 1232, 1242, 1248, 1254, and 1260 are reported. The cost for Aroclor analysis is approximately $200 to $400 per sample (depending on the laboratory and number of samples). The detection limit is approximately 60 to 70 µg/kg (parts per billion soil or sediment [ppb]). The sampling and analysis plan for Aroclor analysis should specify that total PCBs be reported, as this information is important for HHRA and ERA.

2.2 PCB Homologue Analysis

Homologues are groups of PCBs that have the same *number* of chlorines substituted at different positions on the biphenyl ring. Homologues groups in commercial Aroclors can range from no chlorines, where the biphenyl ring is completely unsubstituted, to 10 chlorines (deca-chlorobiphenyl), where all possible positions on the biphenyl ring are substituted with chlorines. Figure A-2 presents the weight percentage of each homologue group that is present in original Aroclor commercial mixtures. It is noteworthy that higher chlorinated homologue groups increase as a percentage of Aroclors from Aroclor 1221 to 1260.

Compared with Aroclor analysis, homologue analysis provides more chemical-specific information regarding the groups of PCBs present at the site. However, homologue information is limited with regard to identifying specific PCB congeners.

Although homologue data (in conjunction with Aroclor data) can be used to gauge the relative extent of weathering, it may not provide the necessary information for an HHRA or ERA because it does not provide quantitative information on specific PCB congeners, particularly the dioxin-like PCB congeners. Homologue data is reported for the total concentration of PCB congeners within the homologue group. However, many PCB congeners are present within each homologue group. Because some may produce dioxin-like effect and others non-dioxin like effects and the inherent toxicity of each individual congener can vary over several orders of magnitude, it is important to determine the concentration of dioxin-like PCB congeners. Absent specific PCB congener information, homologue data can only provide a gross picture of the relative concentrations of different PCB *groups* present at the site. Despite these shortcomings, homologue analysis does provide several advantages over Aroclor analysis.

As mentioned previously, Aroclor analysis can lead to overestimating or underestimating PCB concentrations at the site because it relies heavily on subjective interpretation of the chromatogram “fingerprint” reviewed by the analytical chemist. Weathering of the Aroclor mixture can alter the appearance of the fingerprint, which can result in a false negative result and lead to underestimating total PCB concentrations. In contrast, homologue analysis reduces the possibility of underestimating total PCBs because homologue groups are directly identified in chromatograms and are not subjectively interpreted. Additionally, since each homologue group is directly identified, the possibility of “double counting” PCB congeners (which can occur with Aroclor analysis) is improbable. Consequently, if it is determined that ARARs will not be based on Aroclors, but rather total PCBs, homologue analysis provides superior chemical-specific information regarding PCB levels at the site. For that reason, homologue analysis should be considered the preferred cost-effective screening tool (if Aroclor information is not specifically required), as shown in Table A-3.

2.3 PCB Congener Analysis

Although Aroclor analysis was historically used to evaluate PCB sites, PCB congener analytical techniques have been improved to the point that PCB congener data is far superior because it identifies individual PCB congeners. Each congener can be detected in the parts-per-quadrillion range, which is several orders of magnitude lower than Aroclor analysis. For this reason, PCB congener analysis is commended if it is necessary to conduct an HHRA or ERA. PCB congener analyses circumvent problems encountered with Aroclor analyses, such as false negative results due to weathering. The major drawback of PCB congener analysis is the increased cost over Aroclor or PCB homologue analyses. PCB congener analysis ranges between $900 and $1,200, depending on sample matrix, number of samples, and degree of quality assurance and control required.

Unlike Aroclor analysis, which is confounded by weathering involving preferential degradation and partitioning in environmental media, PCB congener analysis can directly measure all 209 congeners if necessary. Indeed, PCB congener analyses are used to determine the extent of weathering, which is represented by the difference in PCB congener composition between the original Aroclor and the weathered PCB mixture. Congener analyses yield raw data that can be used to develop a site-specific fingerprint of PCBs that can be used to determine sources areas and apportion responsibility for the release when it can be shown different sources have different fingerprints. Statistical methods—including cluster analysis, principal component analysis, and correlative linear regression—can be used to compare site-specific PCB mixtures to point and non-point sources. Congener-specific analysis is also necessary to conduct an HHRA or ERA because weathered mixtures may be enriched in some highly toxic congeners (due to differential environmental partitioning) that would not be accounted for with Aroclor analysis. For example, the toxicity of some non-ortho coplanar PCBs (which are resistant to degradation) can be several orders of magnitude greater than ortho-substituted PCBs. There are numerous analytical methods for PCB congeners, which are summarized in Table A-4. The cost presented for each analysis is a rough estimate intended only for purposes of comparison between methods. Despite the myriad methods available, all congener methods are based on the same high-resolution gas chromatograph methods. Altering any of the methods involves an additional step during calibration. To quantify some congeners (e.g., 77 and 126), a specialized clean-up step is necessary. Selection of a particular method in Table A-4 is based on the intended data use(s) by the project team. Overall, there are two methods for analyzing congeners—namely, *EPA SW 846 Method 8082* and *EPA Method 1668*. If data are to be used for background analyses, it is preferable to analyze for as many PCB congeners as possible with Method 1668 in order to derive the most accurate fingerprint. Method 1668 is also preferable if an HHRA or ERA is performed. This method will quantify the 12 or 13 individual dioxin-like PCB congeners as identified by U.S. EPA and the World Health Organization (WHO).

Table A-4. Methods For PCB Congener Analysis

EPA METHOD	CONGENERS ANALYZED [a]	COST PER SAMPLE	DETECTION LIMIT	
			Soil/Sediment	Water
1668- Rev A	PCB Congeners – WHO '94 (13)	$900-$1200	low ng/kg	low pg/L
1668-Rev-A	PCB Congeners – WHO '97 (12)	$900-$1200	low ng/kg	low pg/L
1668	PCB Congeners – NOAA Status & Trends (18)	$900-$1200	low ng/kg	low pg/L
1668	PCB Congeners – USEPA BTAG List Region IX (28)	$900-$1200	low ng/kg	low pg/L
1668	PCB Congeners – USACE Inland Testing Manual (ITM) (26)	$900-$1200	low ng/kg	low pg/L
1668	STL Environmentally Significant Congener List (56)	$900-$1200	low ng/kg	low pg/L
1668	PCB Congeners (209)	$900-$1200	low ng/kg	low pg/L
1668	PCB Congeners – WHO '94 (13)	$900-$1200	low ng/kg	low pg/L
8082	PCB Congeners – WHO '94 (13)	$200-$400	low µg/kg	low ng /L
8082	PCB Congeners – WHO '97 (12)	$200-$400	low µg/kg	low ng /L
8082	PCB Congeners – NOAA Status & Trends (18)	$200-$400	low µg/kg	low ng /L
8082	PCB Congeners – USEPA BTAG List Region IX (28)	$200-$400	low µg/kg	low ng /L
8082	PCB Congeners – USACE Inland Testing Manual (ITM) (26)	$200-$400	low µg/kg	low ng /L
8082	STL Environmentally Significant Congener List (54)	$200-$400	low µg/kg	low ng /L
1613	Dioxins and Furans	$400	pg/kg	pg/L

Notes: Costs are approximate and are presented only for comparison purposes.
(a) Number in parentheses indicates the number of congeners reported
µg/kg – microgram per kilogram, parts per billion (ppb)
ng/kg – nanogram per kilogram, parts per trillion (ppt)
pg/kg – picogram per kilogram, parts per billion (ppq)

2.3.1 Dioxin-like PCB Congener Analysis

A small subset of PCB congeners evoke dioxin-like PCB toxic effects, which should be target analytes if an HHRA or ERA will be conducted. There are 13 different PCB congeners in this group that have been identified by Ahlborg et al. (1994) and U.S.EPA (1996) that are structurally similar to chlorinated dibenzo-p-dioxins (CDDs) and CDFs. They were present in Aroclors 1242, 1248, 1254, and 1260 in concentrations shown in Table A-5. Like dioxin, these PCB congeners all bind to the aryl hydrocarbon receptor and elicit dioxin-specific biochemical and toxic responses. These toxic responses are exacerbated because these congeners have a long half-life in the body (for many decades), and persist and accumulate in the food chain. Ahlborg, et al. (1994) have derived toxic equivalency factors (TEF) for each of the 13 congeners as a fraction of the toxicity of 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) (further discussed in Part B of this document).

The analytical method for dioxin-like PCB congeners is *EPA Method 1668, Revision A*, as presented in Table A-4. This method is used for water, soil, sediment, biosolids, tissue, and other sample matrices, and utilizes high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). As noted in this table, the dioxin-like PCB congeners are the principal targets for risk assessment purposes; however, the remaining 197 PCB congeners (or any subset) can also be identified for the purpose of fingerprinting.

Table A-5. Dioxin-Like PCB Congener Concentrations In Aroclor Mixtures

PCB CONGENER NUMBER [1]	CONCENTRATION OF DIOXIN-LIKE PCB CONGENERS IN AROCLORS			
	Aroclor 1242	Aroclor 1248	Aroclor 1254	Aroclor 1260
PCB 61	159	305	<4	<55
PCB 77	1700	2990	200	<61
PCB 105	2670	13600	32100	245
PCB 114	328	1829	2460	28
PCB 116	3620	19900	75800	4470
PCB 123	63	260	560	<20
PCB 126	16	38	88	<52
PCB 128	274	1740	23900	17400
PCB 138	1090	6670	116000	152000
PCB 158	36	387	7610	2940
PCB 157	19	101	3410	NA
PCB 166	4	20	211	<16
PCB 167	20	185	4390	1900
PCB 169	<12	>2	<3	<42
PCB 170	39	702	7910	35000
PCB 189	<7	11	268	885

Notes: Adapted from Schwartz et al. (1993)
(1) Dioxin-like PCB congeners identified by EPA (1996)
< : Denotes less than detection limit
Congeners in parts per million (µg/g Aroclor)
Concentrations are approximate due to ranges in different Aroclor formulations

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3.0 IMPURITIES IN PCB MIXTURES

Commercial Aroclor mixtures were produced in such a manner that significant impurities were introduced during the manufacturing process. The most toxicologically important impurities are chlorinated dibenzofurans (commonly referred to as furans), which are as persistent in the environment as PCB congeners. As with PCB congeners, there are numerous individual furan congeners. There are 135 individual furan congeners, of which 10 exhibit dioxin-like toxic properties nearly as toxic as those exhibited by dioxins themselves. For example, 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF) is just one tenth less toxic than 2,3,7,8-tetrachlorodibenzodioxin (2,3,7,8-TCDD). Therefore, if it is thought that Aroclors were released, a limited number of samples should be analyzed for furans due to their toxicity. That is, chlorinated furans produce the same toxic responses and pose the same carcinogenic potential as the dioxins do. Analytical results for furans should be presented together with PCB congener information (and that for dioxins, if present) in an HHRA and ERA because those risks are additive. Table A-6 presents a summary of several studies prepared by WHO (1993) showing the concentration of furans in different Aroclors, which can be relatively high.

Table A-6. Chlorinated Furan Impurities In Commercial Aroclors

AROCLOR MIXTURE	CHLORINATED FURANS IN AROCLORS			
	Tetra Chlorinated Furan [4]	Penta Chlorinated Furan [5]	Hexa Chlorinated Furan [6]	TOTAL
AROCLOR 1248	0.5 (25)	1.2 (60)	0.3 (15)	2.0
AROCLOR 1254	0.1 (6)	0.2 (12)	1.4 (82)	1.7
AROCLOR 1254	0.2 (13)	0.4 (27)	0.9 (60)	1.5
AROCLOR 1260	0.1 (10)	0.4 (40)	0.5 (50)	1.0
AROCLOR 1260	0.2 (25)	0.2 (38)	0.3 (38)	0.8

Notes: Values expressed as mg furans/kg PCB Aroclor.
Values in parentheses represent the percentage of total CDBFs. Values in brackets represent number of chlorines in furans.
Reference: WHO 1993

EPA Method 1613 was developed by USEPA for congener-specific analysis of the tetra through octa-chlorinated furans in aqueous, solid, and tissue matrices by isotope dilution (using HRGC/HRMS). The limits of detection of EPA Method 1613, which is based on analysis of 17 toxicologically significant furans and dioxins, is in the very low parts-per-quadrillion. The analytical cost per sample is approximately $40

4.0 PCB FATE AND TRANSPORT

An understanding of the fate and transport of Aroclors or *de novo* PCBs in the environment is fundamental for establishing data quality objectives (DQOs) and developing a robust sampling plan that targets the appropriate PCB analysis to address site-specific issues.

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4.1 Weathering

It is important that weathering of the original Aroclor be considered at Navy sites because Aroclors were likely released decades ago and have undergone extensive weathering. While some PCB congeners are somewhat susceptible to biodegradation in the environment, other congeners are highly resistant and will persist unchanged for many decades. Although PCBs as a group are not considered water soluble, some congeners are more water-soluble than others, which can result in the more soluble congeners migrating away from the original area where they were released. In contrast, some PCB congeners strongly adsorb to organic material and are virtually immobile. All of these differences result in what is termed “preferential persistence,” in which different congeners partition in different environmental media. This confounds PCB investigations because it can dramatically alter the original Aroclor composition over time.

Partitioning refers to the processes resulting in different PCB congeners separating into air, water, sediment, and soil. As a general rule, PCBs that strongly adsorb to organic content in sediments, soils, and accumulate in biological tissue are more chlorinated. In contrast, congeners with low chlorine content tend to be relatively more volatile and water soluble. Low-molecular weight PCBs can volatilize or disperse as aerosols. Differences in environmental partitioning between different PCB homologue groups can vary over several orders of magnitude.

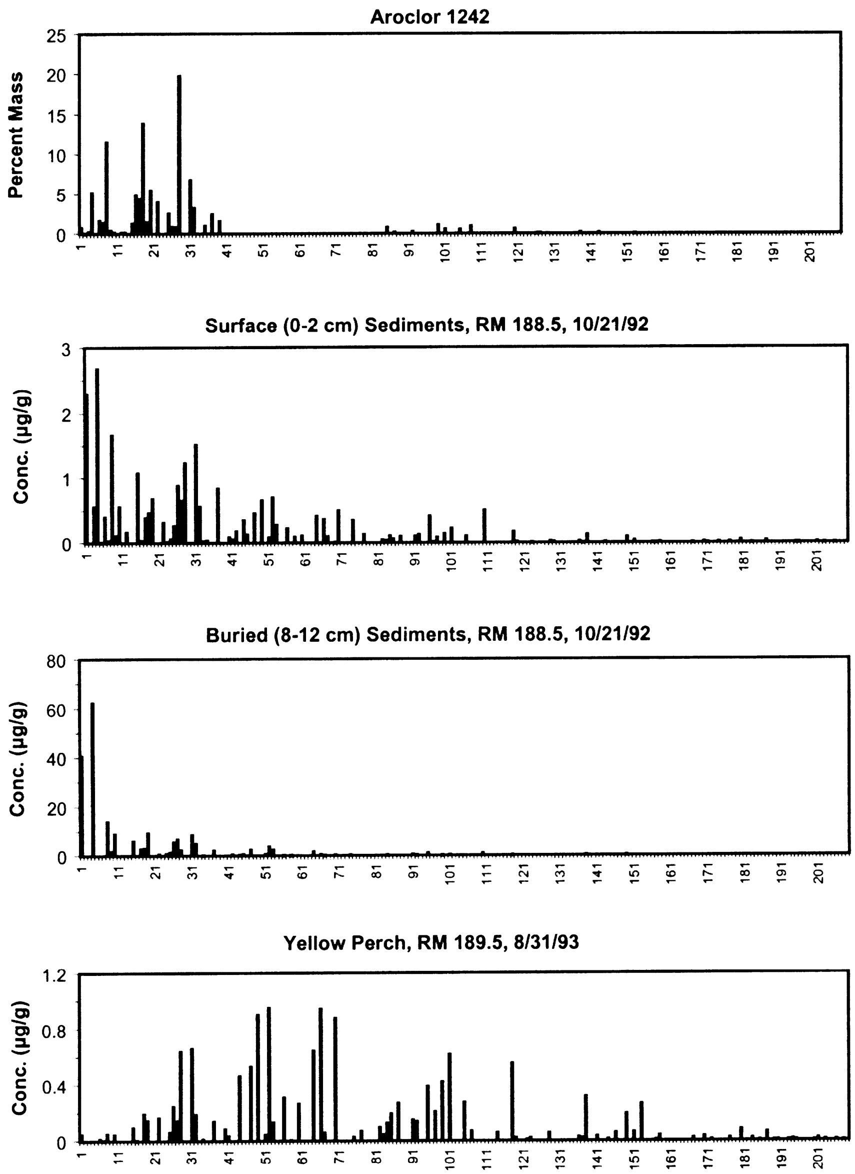
Biodegradation of PCB congeners also modifies the chemical composition of PCB mixtures in the environment. Anaerobic bacteria in sediments selectively remove chlorines and appear to reduce the toxicity and bioaccumulation potential of weathered PCB mixtures. However, dechlorination is not synonymous with detoxification, as congeners having greater carcinogenic potential activity can be formed through dechlorination.

PCBs with higher chlorine content are extremely resistant to oxidation and hydrolysis. This group includes the most toxic fraction of PCB mixtures. Degradation can also occur through photolysis, which can slowly break down congeners with high chlorine content. Despite these processes, however, weathered PCB mixtures persist in the environment for many years.

Living organisms selectively bioaccumulate a subset of PCB congeners. Highly chlorinated PCB congeners are very lipid soluble and are readily absorbed and sequestered into fat tissue by fish and other animals. In contrast, lower-chlorinated PCBs are not as readily absorbed and are eliminated from the body faster. Rates of metabolism and elimination are slow and are congener specific. This is why bioaccumulation in biological systems tends to concentrate congeners of higher chlorine content. The resulting fingerprint of PCBs in tissue samples will be completely different from the original fingerprint of the Aroclor mixture.

Figure A-3 (adapted from NRC 2001) graphically presents how Aroclor composition changes with weathering and how the original Aroclor profile in biological tissues is completely lost. The first frame shows the typical PCB congener profile for Aroclor 1242 represented by mass on the y-axis and each individual congener on the x-axis. The height of each peak shows the relative concentration for each PCB congener from left to right on the graph. Additionally, PCB congeners are increasingly chlorinated moving from left to right. The lower three graphs shows how weathering and preferential partitioning has altered the appearance of Aroclor 1242, which was released into Hudson Bay many decades ago. For example, frame 2 shows how the original Aroclor composition has changed over time in the uppermost 2 centimeters of sediment, where there appears to be a relative increase in higher-chlorinated congeners. This alteration is even more pronounced in fish tissue, as shown in the fourth frame, where there is significant shift in the relative concentration of higher-chlorinated congeners, which are preferentially bioaccumulated. It is clear from this Figure that: (1) The original composition of Aroclor 1242 is significantly altered as it undergoes weathering, and (2) The original congener profile of Aroclor 1242 is completely obscured in fish as only a subpopulation of the higher-chlorinated congeners is preferentially taken up and stored in the tissues. Similar weathering phenomena should be anticipated when investigating Navy installations.

Figure A-3. Aroclor weathering (Nrc 2001)



4.2 Sampling and Analysis of Weathered PCB Mixtures

Environmental samples collected at Navy Installations should be analyzed according to the generalized decision-making framework presented in Table A-3. However, the fate and transport of PCBs should be considered when sampling and analyzing specific environmental media.

As previously discussed, extensively weathered PCBs will not resemble the original Aroclor mixture. Thus, Aroclor analysis should not be used to characterize PCBs releases since the original Aroclor fingerprint will not be preserved. At most Navy sites, the original Aroclor will be substantially altered as to be unidentifiable and require homologue or congener analysis.

Due to the insolubility of PCBs (however, as discussed previously some are more water soluble than others), they will not be detected in surface water or groundwater that is filtered. PCBs that *are* detected will result from suspended sediment particles in unfiltered water samples. This will usually hold true for both surface water and groundwater samples. For this reason, analyzing water samples is of minor importance at most PCB sites unless unusual site conditions exist.

At most sites, analyzing PCBs in biological samples, particularly fish, for estimating ingestion risks in an HHRA or ERA will require PCB congener analysis. Preferential bioaccumulation of a small set of congeners will not likely resemble commercial Aroclor mixtures. When Aroclors are identified, they will not correspond to Aroclors released, but rather to the specific PCB congeners preferentially sequestered in fat deposits in biological tissues. It is particularly important to analyze for dioxin-like PCB congeners because, as a group, they are selectively taken up and retained for long periods of time. Consequently, bioaccumulated PCBs appear to be more toxic than commercial PCBs. Although the rate of metabolism and elimination from biological tissues is dependent on the organism and PCB congeners, the overall rate for PCBs leaving the body is slow.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Potential PCB sites need to first be classified, based on the type of PCB release that may have occurred. PCB sites where PCBs have been formed *de novo* should be investigated differently than sites where Aroclors (or other commercial PCB mixtures) have been released. Although Aroclor analysis was routinely conducted in the past, its use today should be limited to screening sites, particularly Navy sites where the Aroclors have extensively weathered.

Although screening-level Aroclor analysis is the least expensive type of analysis, it provides little information that will be necessary for subsequent investigations, which will likely include background analysis, as well as HHRAs and ERAs. Aroclors undergo significant weathering, changing the original congener composition to the extent that the mixture no longer appears to be the original Aroclor (or, in some cases, *any* Aroclor), thus confounding analyses with false negative errors.

PCB congener data provide the most useful and detailed data of all three PCB analyte groups, but it is relatively expensive. Therefore, statistical analyses are available to limit the number of congener analyses that need to be performed. These statistical approaches are the most cost-effective steps the project team can implement. The statistical results are scientifically tenable and should be implemented by the project team to reduce analytical costs.

In addition to PCBs, CDFs should always be analyzed where Aroclors have been released. As contaminants in the original Aroclor mixture, they will be released along with other PCBs and will partition in the environment similarly to the highly chlorinated PCB congeners.

6.0 REFERENCES

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APPENDIX A:
PCB Congener Composition for all 209 in 5 Aroclors

PCB CONGENER NUMBER (IUPAC No.)	AROCLOR (Percent Weight)				
	1016	1242	1248	1254	1260
1	.52	.54	.05	.02	.02
2	.02	.03			
3	.15	.18	.01		
4	3.62	3.08	.32	.02	.02
5	.17	.14	.00		
6	1.64	1.43	.13	.01	.01
7	.29	.26	.02		
8	8.29	7.05	.81	.05	.04
9	.58	.50	.04		
10	.23	.20			
11					
12	.07	.06			
13	.24	.22	.02		
14					
15	2.40	2.10	.22	.01	.01
16	3.88	3.14	1.04	.02	.01
17	3.98	3.13	1.05	.02	.02
18	10.86	8.53	4.29	.08	.05
19	.99	.80	.22		
20	.88	.72	.14		
21	NM	NM			
22	3.50	2.84	1.33	.02	.01
23	.01	.01			
24	.16	.13	.01		
25	.72	.59	.11		
26	1.57	1.28	.40		
27	.51	.41	.12		
28	8.50	6.86	3.59	.06	.03
29	.10	.08	.00		
30	.00				
31	9.32	7.34	5.07	.11	.04
32	2.37	1.90	.88	.01	.01
33	6.21	5.01	2.23	.05	.03
34	.03	.02	.00		
35	.05	.08	.00		

PCB CONGENER NUMBER (IUPAC No.)	AROCLOR (Percent Weight)				
	1016	1242	1248	1254	1260
36					
37	1.02	2.03	.79	.01	.01
38					
39					
40	.58	.76	1.13	.15	
41	.76	.68	.77	.02	
42	1.59	1.19	1.67	.09	.01
43	.28	.18	.30		
44	4.47	3.55	6.31	.67	.03
45	1.23	.89	1.09	.02	
46	.49	.36	.47		
47	1.26	.93	1.49	.07	
48	1.61	1.18	1.66	.05	
49	3.35	2.53	4.12	.26	.01
50	.01	.00			
51	.32	.23	.30		
52	4.63	3.53	6.93	.83	.24
53	.95	.71	1.05	.04	
54	.01	.01			
55		.10	.06		
56	.07	1.81	3.16	1.70	.02
57	.01	.02	.02		
58					
59	.41	.32	.37	.01	
60	.04	1.18	1.85	.95	.04
61					
62					
63	.06	.12	.17	.07	
64	1.87	1.70	3.01	.36	.01
65					
66	.39	3.39	5.84	3.56	.02
67	.06	.16	.13	.01	
68					
69	.00				
70	.59	3.73	7.28	6.83	.04
71	1.16	1.03	1.67	.11	.01
72	.00	.01	.02		
73	.00	.00			
74	.33	1.81	3.14	2.19	.05

PCB CONGENER NUMBER (IUPAC No.)	AROCLOR (Percent Weight)				
	1016	1242	1248	1254	1260
75	.06	.04	.08		
76		.08	.13	.03	
77		.31	.41	.20	
78					
79					
80					
81		.01	.01	.00	
82		.26	.81	1.53	
83		.11	.26	.56	.01
84	.05	.41	1.26	1.58	.11
85		.31	.98	2.49	.01
86		.03	.11	.10	
87		.46	1.45	3.41	.41
88		.00	.02		
89		.09	.20	.11	
90			NM	NM	
91	.06	.21	.63	.53	.01
92		.09	.38	.57	.30
93		.00	.04		
94		.01	.03	.01	
95	.31	.61	1.96	1.84	2.45
96	.04	.03	.08	.01	
97		.38	1.22	2.78	.09
98					
99	.01	.46	1.47	4.53	.04
100					
101	.04	.69	2.22	5.49	3.13
102	.04	.07	.19	.09	
103			.02		
104					
105	.00	.47	1.60	7.37	.22
106					
107					
108					
109		.06	.18	.78	.01
110		.83	2.97	8.42	1.33
111					
112					
113				.01	

PCB CONGENER NUMBER (IUPAC No.)	AROCLOR (Percent Weight)				
	1016	1242	1248	1254	1260
114		.04	.12	.50	
115		.04	.11	.37	
116					
117		.03	.09	.19	
118		.66	2.29	13.59	.48
119			.06	.12	
120					
121					
122		.01	.06	.25	
123		.03	.07	.32	
124		.03	.10	.47	.01
125		.02	.04	.03	
126			.00	.02	
127					
128		.02	.12	1.71	.53
129			.02	.39	.14
130			.04	.50	.22
131				.14	.07
132		.04	.15	1.50	2.90
133					.07
134				.20	.34
135			.04	.28	1.08
136			.05	.24	1.46
137			.03	.52	.02
138		.10	.38	5.95	6.54
139				.14	
140					
141		.01	.07	.69	2.62
142					
143					
144				.12	.61
145					
146			.04	.45	1.15
147				.02	
148					
149		.06	.24	1.82	8.75
150					
151			.04	.22	3.04
152					

PCB CONGENER NUMBER (IUPAC No.)	AROCLOR (Percent Weight)				
	1016	1242	1248	1254	1260
153		.06	.23	3.29	9.39
154				.02	
155					
156		.01	.06	1.13	.52
157			.01	.30	.02
158		.01	.04	.90	.58
159					
160					
161					
162					
163		.01	.06	.70	2.42
164			.02	.31	.69
165					
166				.05	
167			.01	.35	.19
168					
169					
170				.35	4.11
171				.08	1.11
172				.03	.70
173					.10
174				.14	4.96
175					.17
176				.01	.59
177				.08	2.57
178					.83
179				.02	2.03
180			.02	.42	11.38
181					.01
182					
183				.09	2.41
184					
185					.55
186					
187				.09	5.40
188					
189				.01	.10
190				.05	.82
191					.17

PCB CONGENER NUMBER (IUPAC No.)	AROCLOR (Percent Weight)				
	1016	1242	1248	1254	1260
192					
193					.53
194					2.07
195					.84
196					1.09
197					.07
198					.10
199					1.78
200					.25
201					.24
202					.33
203					1.40
204					
205					.10
206				.03	.53
207					.05
208				.01	.13
209					NM
Sum of Weight Percent	100.0	100.0	100.2	100.2	100.3

Notes: IUPAC- International Union of Pure and Applied Chemists
Blank values indicate "not detected." Values shown as "NM/p" indicate congeners which were "not measured" but are "believed present" based on other studies.
Data adapted from: Frame, G. M., Cochran, J. W., and Boewadt, S.S., J. High Res.* Chromatogr.*, Vol. 19, pp 657-668 (1996).

APPENDIX B

Statistical Correlation Methods To Reduce Sampling Costs For Dioxin-Like Analysis

This section will provide detailed procedures for the statistical correlation protocol used to reduce sampling costs for conducing dioxin-like PCB analysis. This Appendix is currently in preparation.